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This new process, for which Letters Patent have been granted in the United States, Great Britain, Canada and Newfoundland, may be understood from the specification of the British patent, given below, to which are appended a series of explanatory notes and comments. The date of the patent in Canada is Jan. 14, 1869, in the United States, Feb. 9, 1869, and in the United Kingdom, Aug. 13, 1869.

SPECIFICATION.

1. For the extraction of copper from its ores by this process it should be in the state of an oxyd or some compound thereof, as oxychlorid or carbonate. These oxydized forms of copper are decomposed under proper conditions by protochlorid of iron, with the production of dichlorid of copper, which is soluble in certain saline solutions, and in some cases a portion of protochlorid of copper, together with insoluble peroxyd of iron, and more or less insoluble oxychlorid or basic persalt of iron, which may be rendered soluble by the action of sulphurous acid.

2. The naturally or artificially oxydized ores are to be digested with a watery solution of neutral protochlorid of iron, with or without the addition of an earthy or alkaline chlorid, as common salt. The neutral protochlorid of iron may be conveniently prepared by double

decomposition of protosulphate of iron with an equivalent of chlorid of calcium or chlorid of sodium. In preparing the solution, hereinafter designated as the bath, we may proceed as follows :

3. One hundred and twenty (120) pounds of sea salt, or one hundred and twelve (112) pounds of dry chlorid of calcium, or its equivalent of hydrated chlorid, are to be dissolved with two hundred and eighty (280) pounds of protosulphate of iron, (green copperas,) in one hundred (100) imperial gallons of water. In place of the above salts we may substitute an amount of protochlorid of iron prepared by any other method, containing fifty-six (56) pounds of metallic iron. To the bath prepared in either way, two hundred (200) pounds of sea salt are then added, when the solution is ready for use, and will be found capable of chloridizing and dissolving about ninety (90) pounds of copper. The power of brine to dissolve the dichlorid of copper formed increases greatly with the strength and temperature. The proportions above given are convenient, but in the case of poor ores, a solution of one-half the strength may be used with advantage.

4. In the treatment of copper ores by this process, they may be divided into two classes, non-sulphuretted and sulphuretted ores.

5. The first class or non-sulphuretted oxydized ores, includes the native oxyds of copper, the carbonates, and the oxychlorid. To prepare these for treatment they should be finely pulverized, and the carbonates may with advantage be gently calcined before or after grinding, in order to expel carbonic acid. The red oxyd, if alone or greatly predominating, should also be gently calcined after grinding to convert it into protoxyd; but if it be mixed with a considerable proportion of protoxydized ore this is not necessary.

6. The pulverized oxydized ores thus prepared are to be digested in the above bath, with frequent agitation. Heat is not necessary, but it accelerates the solution of the oxyd of copper, which in practice should not be more than sufficient to yield sixty or seventy pounds of copper to the above bath of one hundred gallons. When the solution is complete and the liquid drawn off, the insoluble residue should be lixiviated with a small volume of hot strong brine. The liquid is then digested with metallic iron, by which the copper

is thrown down as cement copper, two parts of iron yielding three parts of metallic copper.

7. The bath thus freed from copper contains a large amount of regenerated protochlorid of iron, and can be used at once to treat a fresh portion of oxydized ore. A small loss of chlorine, which separates as oxychlorid of iron, has, however, to be supplied by adding to the bath, from time to time, protochlorid of iron or the salts required to produce it. This need not, however, exceed for each repetition, one-eighth of the original quantity, and by careful exclusion of the air the quantity to be added each time may be reduced to much less. The strength of the bath in protochlorid of iron should be determined from time to time by appropriate tests.

8. In localities where it may be desirable to economize the protochlorid of iron a modification of the process may be adopted, which consists in treating with sulphurous acid the iron compounds precipitated by the oxyd of copper. To this end sulphurous acid from the roasting of sulphuretted ores, or from any other source, may be made to pass over or through the bath after or during the process of dissolving the oxyd of copper. In this case the protosalts of iron are constantly regenerated, and serve to chloridize fresh portions of oxyd of copper. A small amount of protochlorid of iron, with the aid of sulphurous acid, may, in this modification, be used to convert a large quantity of copper into dichlorid, the excess of which is precipitated, and may be washed out with hot strong brine. As this deposits a large quantity in cooling, the same brine may be employed indefinitely for dissolving dichlorid by heating and cooling it each time.

9. The solid dichlorid is rapidly reduced by contact with metallic iron, especially when wet with brine, and yields metallic copper and protochlorid of iron, one part of iron giving two of copper. To prevent any precipitation of oxychlorid of copper from the dichlorid solution by the air, it is well in all cases to have a small portion of protosalt of iron present. A little free sulphurous acid will also prevent such precipitation; but any excess of this gas should be expelled or allowed to escape from the solution before adding metallic iron.

10. In the case of sulphuretted ores, the first step in the application of our process has for its object to convert the metal into an oxyd soluble in the bath already described. This conversion is effected by calcination in the air, by which means all copper, iron and sulphur are oxydized. [Pyritous ores, holding much iron and sulphur, may be roasted in kilns, then ground and recalcined, but native sulphurets, rich in copper, or regulus, should be ground before calcination, which is best done in a muffle furnace. In either case] a low red heat suffices, and what is called a dead roast is to be avoided, not only because it involves a waste of time and fuel, but because the high temperature renders a portion of the oxyd of copper insoluble in the protochlorid of iron bath. The roasting need be continued only until the complete oxydation of the sulphuret of copper, and its conversion into a mixture of oxyd with a variable proportion of sulphate of copper. This product may be treated directly with the bath, without addition, as directed for non-sulphuretted ores, but the excess of sulphates thus introduced renders the bath impure, and much more metallic iron is required for the subsequent precipitation than when the whole of the copper is in the form of oxyd.

11. We therefore prefer to proceed as follows : We determine in the roasted ore the amount of copper present as sulphate, which will vary very little for any given ore roasted under constant conditions, and we add thereto an equivalent of lime, which gives rise to insoluble sulphate of lime and oxyd of copper. In practice it is well to leave undecomposed a small amount of sulphate of copper, which, in a subsequent stage of the process, will give with metallic iron the sulphate of iron required to replace the small loss already mentioned as occurring when sulphurous acid is not used. To an ore, for instance, with eight per cent. of copper, which after roasting contains three per cent. of copper as oxyd, and five per cent. as sulphate, we may add lime enough to decompose four-fifths of the latter, at the rate of 28·0 parts of pure lime for 31·7 parts of copper, or about an equal weight of ordinary non-magnesian lime ; being four pounds of finely ground lime for each one hundred pounds of the above roasted ore. An equivalent quantity of carbonate of lime, or other alkaline or earthy base, may be used instead of quick-lime, but with less advantage. The roasted ore and lime may be

added to the bath together, or better, the ore is to be added first. The subsequent part of the process is to be conducted as already described for the ores of the first class.

12. When protosulphate of iron is used instead of the protochlorid in preparing the bath, or in keeping up its strength, as in the case of ores of the first class, sulphate of soda is formed, which may in great part be crystallized out by extremes of heat and cold. The formation and accumulation of this sulphate may, however, be prevented by the use of chlorid of calcium as already set forth. The still larger production of sulphate of soda, which would take place if calcined ores of the second class were added directly to the bath, is prevented by the use of lime as already described, and that portion which must result from the excess of sulphate of copper, as recommended, may be decomposed by the addition of small portions of chlorid of calcium from time to time. By attending to these precautions the strength of the bath in chlorid of sodium, and its solvent power may be indefinitely maintained.

13. We do not claim the use of any particular form of furnace, nor of any special arrangement for calcining, lixiviating or precipitating, reserving to ourselves the choice of the best forms of apparatus for these purposes; neither do we claim the use of protosalts of iron otherwise than in solution, nor the use of perchlorid or other persalts of iron, nor yet the use of sulphurous acid save and except in connection with protosalts of iron, as already set forth.

14. What we claim as our invention is :

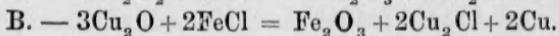
I. The use and application of a solution of neutral protochlorid of iron, or of mixtures containing it, for the purpose of converting the oxyd or suboxyd of copper, or their compounds, into chlorids of copper.

II. The use of sulphurous acid for the purpose of decomposing the oxychlorid of iron formed in the preceding reaction.

III. The use of a process for the purpose of extracting copper from its naturally or artificially oxydized compounds by the aid of the first, or the first and second of the above reactions, substantially in the manner already set forth.

EXPLANATIONS.

Chloridizing the Copper.—The reaction between protoxyd of copper and protochlorid of iron gives rise to peroxyd of iron, and a mixture of the two chlorids of copper, two thirds being as dichlorid, and one third as protochlorid of copper, as shewn in the equation A. The red oxyd or dinoxyd of copper in like manner gives rise to peroxyd of iron, but yields a mixture of two thirds dichlorid and one third of metallic copper, as shown in the equation B.

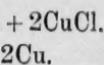


Inasmuch as the metallic copper (2Cu) set free in B. is readily converted into dichlorid by the protochlorid, (2CuCl) of A, it follows that if not more than one half of the copper be dinoxyd, the remainder being protoxyd, the whole will be chloridized by the action of the protochlorid of iron bath.

Solubility of the Dichlorid of Copper.—While the protochlorid of copper is very soluble, the dichlorid is insoluble in water, but readily soluble in a strong solution of sea-salt, and of most other chlorids. A saturated brine at a temperature of 194° Fahrenheit, (90° Centigrade,) will hold in solution more than 16 per cent. of dichlorid of copper, and at 104° F. (40° C.,) more than 8 per cent. A brine containing fifteen parts of salt to one hundred of water, dissolves at 194° F. (90° C.) 10·0 per cent., at 104° F. (40° C.) 6·0 per cent., and at 57° F. (14° C.) 3·5 per cent. of dichlorid of copper. When these strong solutions are diluted with water they deposit much of the dichlorid as a white crystalline powder. A solution made with five parts of salt to one hundred of water, dissolves at 194° F. (90° C.) only 2·6 per cent., and at 104° F. (40° C.) only 1·1 per cent. of dichlorid of copper. The above figures are approximate and a little below the results of actual experiment. 100 parts of dichlorid contain 64 parts of metallic copper.

Composition of the Bath.—The equivalent weight of protosulphate of iron or copperas is 139, and that of common salt 58·5,

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while that of copper is 3·17, and that of iron 2·17. The proportions for the bath, numbers a little given, to allow for impurities in the salts employed. Three equivalents, say 95·1 pounds of copper, of protoxyd, two equivalents of protochlorid of copper from 280 pounds of copperas and 120 pounds of water. Convert one third of the copper into protochlorid of dichlorid, equal to 98·9 pounds of dichlorid of copper. This soluble we have prescribed the addition of 100 imperial gallons or 1000 pounds of water. In converting one third of the copper into protochlorid of dichlorid, equal to 98·9 pounds of dichlorid of copper. This soluble we have prescribed the addition of 100 imperial gallons or 1000 pounds of water. In holding but 15 per cent., will dissolve at 194° Fahrenheit, than this quantity. While these are the theoretical proportions, in practice, from a secondary re-action resulting from an insoluble basic per-salt, a loss of protochlorid of copper will occur, amounting to from five to ten per cent., so that the amount of salt added to the bath is somewhat less than above represented. If a considerable portion of dinoxyd of copper be present, the amount of dichlorid will be larger than above calculated. On account of these reasons it is not well to add to the amount of salt more than 60 or 70 pounds of copper for each 100 gallons of water. The copper from a properly prepared ore will be dissolved by several hours digestion or percolation, even more rapidly in proportion as the heat approaches 194° Fahrenheit.

Preparation of the Ores.—In the calcination of sulphuretted ores recommended, the object is to expel the carbonic acid gas which would otherwise cause much effervescence in the bath. As the dinoxyd predominates in the ore, this should be converted into protoxyd by calcination in the air, which latter, when heated, leaves one third of its copper undissolved in the bath. In calcinating sulphuretted ores by roasting till all the sulphur is removed, there is obtained a mixture of sulphate of copper and a portion of dinoxyd, which latter, according to Pfeiffer, amounts to 20 or 30 per cent. of the copper. Farther roasting will convert both this and the sulphate into protoxyd, but this operation is less advantageous, inasmuch as both operations are liable to contaminate the bath.

consumed and the copper is rendered less soluble. The large proportion of dinoxyd, moreover, suffices, as already explained, to convert much of the protochlorid of copper into dichlorid, thereby effecting a saving of iron in precipitating.

Consumption of Metallic Iron.—With few exceptions the copper extracted by solution from its ores is thrown down in the metallic state as cement copper, by means of metallic iron. In theory there are required less than 89 (88.3) parts of pure iron to precipitate 100 parts of copper from a solution of protosulphate or protochlorid, but in practice two or three times as much are consumed. This great consumption of metallic iron is due to two principal causes :

1st. In the ordinary processes for extracting copper from its ores by the moist way, acids (and sometimes persalts of iron) are employed to render the copper soluble, either as the principal agents or as auxiliaries. When these are employed the solutions contain more or less of persalts of iron, which consume the metallic iron that would otherwise throw down the copper. Thus an amount of persulphate holding four equivalents of iron consumes five equivalents of metallic iron, and is thereby converted into protosulphate, depositing at the same time four equivalents of iron in the form of an insoluble basic persuphate, which contaminates the cement copper.

2nd. The second cause of the waste of iron is the action of the air. In order to separate the whole of the copper from the solutions a digestion of several days with metallic iron is resorted to. The protosalts of iron, which is formed in this re-action, greedily absorbs oxygen from the air and is thereby converted into a mixture of an insoluble and a soluble persalt. The latter, as above shown, dissolves a quantity of iron in its turn, and yields another portion of insoluble persalt, which falls with the cement copper.

The result of the above causes combined is that instead of 89 parts of iron there are consumed, according to circumstances, from 200 to 300 parts of metallic iron to produce 100 parts of metallic copper in the form of cement copper. This, too, is rendered impure by an admixture of insoluble persalts of iron, generally amounting to from 20 to 40 per cent., and even more. The present process avoids both of

these faults, and enables us to obtain a pure cement copper with a very small consumption of iron. The solution obtained with the bath of protochlorid of iron can contain no persalt of iron in solution, and if protoxyd of copper alone has been employed will hold three equivalents of copper combined with two equivalents of chlorine, so that they will be precipitated by two equivalents of iron, being at the rate of 59 parts of metallic iron for 100 parts of metallic copper. If, from the presence of much dinoxyd, or from other reasons, the greater part of the copper be present as dichlorid, it will be remembered that this requires only one equivalent of iron to precipitate two equivalents of copper, being at the rate of 45 parts of iron for 100 parts of metallic copper.

The precipitation of copper from the solutions is at first rapid, especially if these are hot, and kept in agitation. Inasmuch as the waste liquors are not rejected in this, as in the ordinary process, the long digestion with iron required to remove the last portion of copper is dispensed with, and the liquid, after having given up the greater part of its metal, is withdrawn and used for the treatment of a fresh portion of ore. The prolonged action of the air on the bath is thus avoided, and we obtain a cement copper almost entirely free from insoluble iron salts, and with the consumption of a minimum quantity of iron.

The Regenerated Bath.—If the action of the air be excluded it will be found that the bath, after complete precipitation of the copper by iron, will be nearly as rich in protochlorid of iron as before the solution of the copper. The loss, which is due to the separation of a portion of oxychlorid of iron during the solution, is variable, and in some cases does not exceed six per cent. The various ways of supplying this loss are three: (1) The direct addition to the bath of a portion of protosulphate or protochlorid of iron. (2) The addition of a portion of sulphate of copper from the roasted ore, and (3) the use of sulphurous acid. Of these the first requires no explanation, and the second and third will be explained under the two following headings. The proportion of iron in the bath should be determined from time to time by the following method: A small portion of the bath, freed from copper by digestion for some hours with metallic iron in a stoppered bottle, is diluted with 50 parts of water,

and strongly acidulated with sulphuric acid. A standard solution of permanganate of potash of known strength is then added from a graduated tube so long as it is decolorized. By comparative experiments of this kind on the regenerated bath its strength in protochlorid of iron is readily determined.

The Protosalts of Iron.—In preparing the bath we have recommended either protosulphate or protochlorid of iron. The former salt, being an article of commerce, is to be obtained in many places where the latter cannot readily be procured, and may be easily manufactured for the purpose in regions where neither of these can be readily obtained, provided sulphuretted copper ores are to be had. It is well known that in roasting these a considerable portion of the copper is converted into sulphate, which may be readily dissolved by water from the roasted ore. If to each 63.4 pounds of copper thus dissolved, we add 120 pounds of common salt, and digest the liquid with metallic iron in a close vessel, best with the aid of heat, till the copper is precipitated, the solution will contain such an amount of protochlorid of iron that it will only be necessary to add 200 pounds of common salt and a sufficient amount of water, to make 100 gallons of the bath of the strength before prescribed.

If a roasted ore, charged with sulphate, be added directly to the bath of protochlorid of iron, it will be found, after precipitating the copper by metallic iron, that the regenerated bath will contain not only the protosalt of iron, corresponding to that originally present in the bath, but also that resulting from the action of the metallic iron on the sulphate of copper introduced, which has given rise to protochlorid of iron and sulphate of soda by double decomposition; thus rendering the bath impure both from the presence of sulphates and from an excess of protochlorid of iron. To obviate these results we add to such roasted ores, (as already described in § 11), so much lime as may be necessary to convert the whole or the greater part of the sulphate of copper present into insoluble sulphate of lime and protoxyd of copper, which latter is at once soluble in the protochlorid bath. A small portion of sulphate of copper as above prescribed, may be left undecomposed by lime, and by its re-action with metallic iron will give the protosulphate of iron required to supply the small loss

already explained, and keep up the regenerated bath to its original standard, as shown by the test with permanganate.

The use of protosulphate of iron for making the bath, introduces a large proportion of sulphate of soda. A large amount of this, it is true, crystallizes out when the bath is exposed to cold, and may thus be got rid of. The use of a portion of chlorid of calcium may also, as already explained, be resorted to with advantage where this substance can be cheaply procured. In districts where hydrochloric acid is a bye-product of little value it will be best to obtain the protochlorid of iron directly by saturating the crude acid with scrap iron and employing the product as already explained in § 3.

Use of Sulphurous Acid.—When the mixture resulting from the action of oxyd of copper upon the bath of protochlorid of iron, is heated and exposed to the action of an excess of sulphurous acid, the whole of the separated peroxyd of iron is converted into a protosalts, and the bath, after precipitation by metallic iron, is found to contain much more protosalts than at first. Such a result is of course to be avoided, but by passing into the bath a small portion of sulphurous acid towards the close of the digestion, it is easy to dissolve such a portion of the precipitated oxychlorid or oxyd of iron as to prevent the loss of iron which otherwise occurs, and keep up the standard of the regenerated bath without the addition of a salt of iron or of sulphate of copper.

Solvent Power of Protochlorid of Copper.—Protochlorid of copper readily attacks metallic copper, forming with it dichlorid. Hence, as already explained, the metallic copper which is separated when the protochlorid of iron bath acts on dinoxyd of copper is at once dissolved if an equivalent of protoxyd of copper be present to yield the requisite amount of protochlorid. The protochlorid of copper will also attack the certain sulphuretted compounds of copper. Copper glance, purple copper ore, or artificial products as regulus approaching these in composition, are readily dissolved by a solution of protochlorid of copper mixed with common salt, dichlorid of cop-

per being formed. Hence, a sulphuretted ore imperfectly roasted, and still containing a small portion of sulphuret, rich in copper, will give it up to the action of a bath containing protochlorid of copper.

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